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Patentanmeldung Nr. Patent application No. Demande de brevet n°

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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

A process for the manufacture of sulphur-containing ammonium phosphate fertilizers

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A PROCESS FOR THE MANUFACTURE OF SULPHUR-CONTAINING AMMONIUM PHOSPHATE FERTILIZERS

FIELD OF THE INVENTION

The invention relates to a process for the manufacture of sulphur-containing ammonium phosphate fertilizers.

The invention further relates to sulphur-containing fertilizers of the ammonium phosphate type, preferably sulphur-containing diammonium phosphate (S-DAP), sulphur-containing mono-ammonium phosphate (S-MAP) or sulphur-containing nitrogen-phosphorous-potassium compounds (S-NPK), obtainable by the process described in the invention.

The invention further relates to the use of these sulphur-containing fertilizers, especially to grow agricultural products on sulphur-deficient soil.

The invention also relates to the agricultural products grown on soil, especially on sulphur-deficient soil which has been treated with the sulphur-containing fertilizers of the present invention.

BACKGROUND OF THE INVENTION

In the past a tremendous amount of work has been devoted to the manufacture of sulphur-containing fertilizers. The growing world-wide demand for sulphur-containing fertilizers stems from the discovery that low crop yields in certain cases may be related to deficiencies in sulphur. An example of a species with high sulphur requirements is Canola. Canola is an important cash crop in Alberta, Canada, and has high sulphur requirements at any growth stage. A shortage of sulphur can cause serious reductions in crop yield.

Manufacturing processes for sulphur-containing

fertilizers of the ammonium phosphate type often involve the use or incorporation of sulphates, see e.g. US 4,377,406, or US 4,762,546.

A disadvantage of sulphates is that they are very mobile in the soil and leachable. It is therefore more advantageous to have the sulphur present as elemental sulphur.

The advantage elemental sulphur has above sulphates is that elemental sulphur is not leached out of the soil as are sulphates.

Furthermore, elemental sulphur offers some additional benefits in fertilizers: elemental sulphur acts as a fungicide against certain micoorganisms, it assists the decomposition of plant residues and it improves phosphorus utilization and reduces the pH of alkaline and calcareous soils.

Thus, it is advantageous to incorporate sulphur as elemental sulphur in the sulphur-containing fertilizers.

Processes for the manufacture of sulphur-containing fertilizers, wherein elemental sulphur is used, are known in the art. Most of the methods involve the incorporation of molton sulphur into the fertilizer.

In US 5,653,782, a process for the manufacture of sulphur-containing fertilizers has been described, wherein a substrate containing fertilizer particles is heated to a temperature above the melting point of sulphur and admixed with sulphur. According to US 5,653,782, the sulphur is melted by the heat provided by the preheated fertilizer particles, thereby producing a homogeneous coating on the fertilizer particles.

In US 3,333,939, fertilizer compositions for use in alkaline soils are described. According to US 3,333,939, fertilizers which can provide a localized environment of

reduced pH can result in a more efficient plant food uptake from the fertilizer.

The fertilizers mentioned in US 3,333,939 are in the shape of granules and are of the urea-phosphate type. These fertilizers are prepared by reacting urea with phosphoric acid to form a ureaphosphate rection product, mixing ammonium phosphate and sulphur with the ureaphosphate reaction product and granulating the ureaphosphate-sulphur mixture.

In US 3,333,939, the sulphur is introduced in a granulator as a liquid under pressure or as a solution of ammonium polysulfide (column 4, lines 49-51 and 54-56).

Alternatively, US 3,333,939 mentions that the sulphur can be introduced into a granulator as part of a stream containing urea, sulphur and granulation nuclei, while phosphoric acid and ammonia are also fed into the granulator.

A disadvantage of the process mentioned in US 3,333,939 is that the sulphur is used in the dry form when mixed to obtain the feed stream. The handling and grinding of dry sulphur is highly hazardous due to the dust and risks of explosions. As mentioned in a review by H.P. Rothbaum et al (New Zealand Journal of Science, 1980, vol. 23, 377), explosion hazards are always due to sulphur dust which is inflammable. Therefore, a more complex process design is necessary to ensure the safety of the process.

Another disadvantage of the processes described in US 3,333,939 is that the sulphur is added separately to the granulator. It will be difficult to control the distribution and the amount of sulphur present in the resulting fertilizer granules. A broad range of particle sizes and even lumps of sulphur may be formed. In order

to obtain a more homogeneous mixture, further grinding and screening will be required. These operations are relatively quite expensive and involve the danger of explosions.

Since many of the findings in the art are conflicting and problems with the manufacture of fertilizers of the ammonium-phosphate type, containing elemental sulphur, continue to be in existence, there is still considerable room to search for a manufacturing process for such fertilizers which would diminish or even prevent the problems experienced in the art.

It has now been found that a process for manufacturing sulphur-containing fertilizers can be employed, wherein elemental sulphur is introduced before the drying step in the manufacturing process.

This process offers advantages compared with conventional manufacturing processes for fertilizers containing elemental sulphur, with regard to safety aspects as well as with respect to process control.

The process according to the invention enables the manufacture of fertilizer products with a controlled range of sulphur which is embedded in a way that enhances conversion in the soil to plant usable form, sulphates, namely in small particles that are evenly distributed throughout the fertilizer product.

The fertilizer product is thus enabled to deliver sulphates to the intended crop in a more reliable and consistent manner.

SUMMARY OF THE INVENTION

The invention therefore relates to a process for the manufacture of sulphur-containing fertilizers comprising the steps of:

(a) mixing ammonia, phosphoric acid and water in a reactor unit to obtain an ammonium phosphate mixture;

(b) introducing the mixture obtained in step (a), optionally with additional ammonia and/or recycled fines, into a granulator unit to obtain granules and
(c) drying the granules obtained from step (b) in a drying unit,
wherein elemental sulphur is introduced before the drying step (c).

The invention further relates to sulphur-containing ammonium phosphate fertilizers, to the use of these sulphur-containing fertilizers to promote the growth of agricultural products and to the agricultural products thus-obtained.

DETAILED DESCRIPTION OF THE INVENTION

In the first step of the process according to the invention, ammonia, phosphoric acid and water are contacted in a reactor unit to obtain an ammonium phosphate mixture. The phosphoric acid referred to herein is typically commercially available phosphoric acid. Suitable phosphoric acids are for example orthophosphoric acid, or pyrophosphoric acid or mixtures thereof. The ammonia is typically introduced as a concentrated aqueous solution or gaseous ammonia. A preferred type of a gaseous ammonia is anhydrous ammonia.

The molar ratio of ammonia and phosphoric acid is typically kept between values of about 0.5-1.0 for the production of S-MAP, typically between values of about 1.2-2.0 for the production of S-DAP and typically between values of about 0.7-1.7 for the production of NPK. Preferred values for the ammonia:phosphoric acid molar ratio's are about 0.6-0.8 for the production S-MAP, 1.3-1.8 for the production S-DAP and about 1.0-1.5 for NPK.

More preferred values for the ammonia:phosphoric acid molar ratio's are about 0.7 for the production S-MAP, about 1.6 for the production S-DAP and about 1.3 for NPK.

Typically, the water content in the ammonium phosphate mixture is kept as low as possible, preferably between appoximately 10 and 20% based on the total weight of the mixture, more preferably between 12 and 15% based on the total weight of the mixture. Reference to the ammonium phosphate mixture herein is to the mixture in step (a) of the process according to the invention. Said mixture can comprise the added elemental sulphur.

The advantage of using a mixture with as little water as possible is that any additional water introduced into a fertilizer process must be handled in the process and eventually eliminated. Therefore, any additional water introduced into fertilizer manufacturing processes leads to a more complex process. In the present invention, a concentrated mixture is used, which enables a more simplified process.

The reactor unit used in step (a) is a device wherein the ammonia, phosphoric acid and water are reacted to obtain an ammonium phosphate mixture.

A suitable reactor unit is for example a pipe cross reactor unit or a preneutralizer unit.

Typically, the mixing takes place at atmospheric pressure.

The mixing can take place at temperatures between about 100 °C and about 130 °C, preferably between 115 °C and 121 °C or between 100 °C and 113 °C. Preferably, water or sulphuric acid is added to the reactor unit to control the temperature of the mixture. Typically, water is added to reduce the temperature, sulphuric acid is added to increase the temperature.

After step (a), a mixture comprising ammonium phosphate is obtained. This mixture is introduced into a granulator.

Reference herein to a granulator is to a device for forming granules or pellets of fertilizer product. Commonly used granulators are described in Perry's Chemical Engineers' Handbook, chapter 20 (1997). Preferred granulators are drum granulators or pan granulators.

Preferably, the mixture is pumped and distributed on a rolling bed of material in a drum granulator.

In the granulator, granules are formed. Reference herein to granules is to discrete particles comprising ammonium phosphate and elemental sulphur.

Optionally, ammonia can be introduced in the granulator to complete the ammoniation of the ammonium phosphate mixture.

Optionally, water and steam can also be fed to the granulator to control the temperature of the granulation process as needed.

In one process according to the invention, the elemental sulphur is introduced into the reactor unit in step (a).

In another process according to the invention, elemental sulphur is introduced into the granulator in step (b).

The elemental sulphur is preferably introduced as a slurry of water and micron-sized sulphur particles. Typically, the micron-sized sulphur particles are dispersed or suspended in the slurry.

The term micron-sized particles used herein refers to sulphur particles having a size ranging from between about 0.5 to about 150 microns, preferably between about 1.0 and about 100 microns.

Typically, the water content in the sulphur slurry is kept as low as possible, preferably between appoximately 10 and 40% based on the total weight of the mixture, more

preferably between 15 and 30% based on the total weight of the slurry.

Preferably, the slurry is stirred or mixed in a suitable apparatus before it is introduced into the manufacturing process.

Typically, the slurry is introduced by pumping the slurry from a sulphur slurry reservoir unit into the reactor unit or into the granulator unit.

Alternatively, the elemental sulphur is introduced as emulsified sulphur particles in water, preferably emulsified micron-sized sulphur particles in water. An advantage of using emulsified micron-sized sulphur particles is that the precipitation of sulphur particles is kept to a minimum. Reference to emulsified sulphur particles herein is to sulphur particles which are kept in suspension through the addition of an emulsifying additive.

In yet another preferred process according to the invention, the elemental sulphur is introduced as molten sulphur. Molten sulphur can be obtained from solid sulphur, by melting in a suitable melting apparatus, for instance a tube melter.

When using a preneutralizer reactor in step (a), the elemental sulphur is preferably introduced as molten sulphur.

When using a pipe cross reactor in step (a), the elemental sulphur is preferably introduced as slurry of water and micron-sized sulphur particles.

The sulphur-containing ammonium phosphate granules obtained after the granulation step are dried in a drying unit. Suitable drying units include drying units wherein heat transfer for drying is accomplished by direct contact between the wet solid and hot gases.

Typically,the drying unit is a rotary dryer.

In a preferred process according to the invention, the granules are sorted on their size in a sorting unit.

Typically, oversized granules are crushed and returned to the sorting unit while undersized granules are returned to the granulator.

A preferred size range for the granules is between about 1.5 and 5.0 mm, more preferably between about 2 and 4 mm, expressed as the average diameter of the granules.

It will be appreciated that the process parameters in the reactor unit and in the granulator unit have to be adjusted depending on the desired products.

Other ingredients may be added during the manufacturing process to tailor the fertilizer products to their intended end-use.

Examples include plant nutrients such as potassium, sodium, zinc, manganese, iron, copper, molybdenum, cobalt, calcium, magnesium and combinations thereof.

These nutrients may be supplied in elemental form or in the form of salts, for examples as sulfates, nitrates or halides. In this way, granules enriched in plant nutrients are obtained.

The amount of plant nutrients depends on the type of fertilizer needed and is typically in the range of between 0.1 to 5%, based on the total weight of the granules.

After a typical manufacturing process according to the invention, sulphur-containig monoammoniumphosphate, sulphur-containing diammoniumphosphate or sulphur-containing NPK (nitrogen-phosphorous-potassium) fertilizers, optionally enriched in plant nutrients, are obtained.

The content of elemental sulphur in these fertilizers

is typically up to 25%, based on the total weight of the fertilizer, preferably between 2 and 18%, more preferably between 5 and 15%..

The sulphur in the sulphur-containing fertilizers according to the invention may be incorporated into the fertilizer granules, or the sulphur may be distributed on the granules or the sulphur may be both incorporated into the granules and be distributed on the granules.

The invention will now be illustrated by means of schematic figure 1.

Figure 1 depicts a typical process scheme of the process according to the invention, wherein the elemental sulphur is introduced in step (a).

Phosphoric acid is led from tank (1) via line (2) to a reactor (3). Gaseous ammonia is led from tank (4) via line (5) to reactor (3). Water is led from tank (6) via line (7) to reactor (3). Sulphur is led from tank (8) via line (9) to reactor (3).

In reactor (3), the anhydrous ammonia and phosphoric acid are reacted to form a sulphur-containing ammonium-phosphate mixture. This mixture is pumped via line (10) to a drum granulator (11), where it is introduced on top of a rolling bed of fertilizer material. Gaseous ammonia is led from tank (4) via line (12) into the drum granulator to increase the mole ratio to approximately 1.8 or 1.0 when producing S-DAP or S-MAP respectively.

In granulator (11), moist sulphur-containing ammonium-phosphate granules are formed. The moist granules are led via line (13) to a rotary dryer 14). In the rotary dryer (14), the granules are dried. The dried granules are led via line (15) to a sizing unit (16).

In the sizing unit, granules that are too large or too small, relative to a pre-determined granules size,

are removed from the granules stream. The oversized granules are led via line (17) to a crusher (18) where they are crushed. The crushed granules are returned via line (19) to the sizing unit. The undersized granules are recycled via line (20) to the granulator. The granules with a size range of between 2.0 and 4.0 mm are led via line (21) to a cooler (22) where they are cooled. A portion of granules with a size range of between 2.0 and 4.0 mm is recycled via line (23) to the drum granulator to help control the granulation process.

Ammonia and water vapors escaping from reactor (3) are led via line (24) to a wet scrubber unit (25), where they are scrubbed with phosphoric acid. The scrubber liquid containing ammonium phosphate is led back via line (26) to reactor (3).

The air and dust collected from the drum granulator, dryer discharge elevator and drum granulator surroundings are led via lines (27) and (28) to a Venturi type scrubber (29) where they are treated and then vented via line (30) to the atmosphere.

The invention will now be illustrated by means of the following non-limiting examples.

EXAMPLE 1 (comparative)

DAP granules without added sulphur were prepared using the process according to schematic figure 1, but without added sulphur from tank (8). A preneutralizer reactor was used as reactor (3). The reaction mixture in the preneutralizer reactor was maintained at 115 °C, with a NH_3:H_3PO_4 mole ratio of 1.42. Chemical analysis of the resulting granules indicated 19.0% N, 50.5% P_2O_5 and 0.9% sulphate sulphur (expressed as weight percentages based on the total weight).

EXAMPLE 2 (according to the invention)

DAP granules with added sulphur were prepared using the process according to schematic figure 1. The reactor

used was a preneutralizer reactor. The reaction mixture in the preneutralizer reactor was maintained at 117 °C, with a NH_3:H_3PO_4 ratio of 1.44. Chemical analysis of the resulting granules indicated 15.7%N, 41.8 %P_2O_5, 0.6% sulphate sulphur and 17.6 % elemental sulphur (expressed as weight percentages based on the total weight). Scanning electron microscopy (SEM) analysis was performed to evaluate if the added sulphur was evenly dispersed in the fertilizer granules. SEM analysis of the granules and of split granules indicated that the sulphur was distributed both on the surface of the granules and throughout the granules.

<u>EXAMPLE 3 (comparative)</u>

MAP granules without added sulphur were prepared using the process according to schematic figure 1, but without added sulphur from tank (8). A pipe cross reactor was used as reactor (3). The reaction mixture in the pipe cross reactor was maintained between 120 and 126 °C, with a NH_3:H_3PO_4 mole ratio of 0.67. Chemical analysis of the resulting granules indicated 11.3% N, 56.0% P_2O_5 and 1.0% sulphate sulphur (expressed as weight percentages based on the total weight).

<u>EXAMPLE 4 (according to the invention)</u>

MAP granules with added sulphur were prepared using the process according to schematic figure 1. The reactor used was a pipe cross reactor. Sulphur was added as emulsified sulphur. The emulsified sulphur was agitated in a container and then transferred directly from the container to the sulphur feed tank (8). The reaction mixture in the pipe cross reactor was maintained at about 122 °C, with a NH_3:H_3PO_4 ratio of 0.69. Chemical analysis of the resulting granules indicated 10.3%N, 50.3 %P_2O_5, 0.7% sulphate sulphur and 11.0 % elemental sulphur (expressed as weight percentages based on the total weight). Scanning electron microscopy (SEM) analysis was performed to evaluate if the added sulphur was evenly dispersed in the fertilizer granules. SEM

analysis of the granules and of split granules indicated that the sulphur was distributed both on the surface of the granules and throughout the granules.

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CLAIMS

1. A process for the manufacture of sulphur-containing fertilizers comprising the steps of:
(a) mixing ammonia, phosphoric acid and water in a reactor unit to obtain an ammonium phosphate mixture;
(b) introducing the mixture obtained in step (a), optionally with additional ammonia and/or recycled fines, into a granulator unit to obtain granules and
(c) drying the granules obtained from step (b) in a drying unit,
wherein elemental sulphur is introduced before the drying step (c).

2. A process according to claim 1, wherein the elemental sulphur is introduced in the reactor unit in step (a).

3. A process according to claim 1, wherein the elemental sulphur is introduced in the granulator unit in step (b).

4. A process according to any one of claims 1 to 3, wherein the reactor unit in step (a) is a pipe cross reactor unit.

5. A process according to any one of claims 1 to 3, wherein the reactor unit in step (a) is a preneutralizer.

6. A process as claimed in any one of claims 1 to 5, wherein the elemental sulphur is introduced as a slurry, of micron-sized sulphur particles in water, the particle size of the sulphur particles preferably being between 0.5 and 150 microns, more preferably between 1.0 and 100 microns.

7. A process as claimed in any one of claims 1 to 5, wherein the elemental sulphur is introduced as molten sulphur, the temperature of the mixture preferably being kept above 113 °C.

8. A process as claimed in any one of claims 1 to 7, wherein overzised granules are sized and crushed and recycling of the fines takes place.

9. A process as claimed in any one of claims 1 to 8, wherein anhydrous ammonia is used.

10. A process as claimed in any one of claims 1 to 9, wherein a drum granulator is used.

11. A process as claimed in any one of claims 1 to 10, wherein a potassium salt and/or other plant nutrients has been added to the fines.

12. Sulphur-containing fertilizers, preferably sulphur-containing diammoniumphosphate, sulphur-containing, monoammoniumphosphate or sulphur-containing fertilizers, nitrogen-phosphorous-potassium, obtainable by a process as described in any one of claims 1 to 11.

13. Sulphur-containing fertilizers as claimed in claim 12, wherein the sulphur content is less than 25% (w/w), preferably between 2% and 18%, more preferably between 5% and 15%, based on the final product.

14. Use of sulphur-containing fertilizers as claimed in claims 12 to 13 to grow agricultural products from soil, wherein the fertilizers are used on soil which is deficient in sulphur.

15. Agricultural products obtained from using the sulphur-containing fertilizers as claimed in claim 14.

ABSTRACT

The invention relates to a process for the manufacture of sulphur-containing fertilizers comprising the steps of:
(a) mixing ammonia, phosphoric acid and water in a reactor unit to obtain an ammonium phosphate mixture;
(b) introducing the mixture obtained in step (a), optionally with additional ammonia and/or recycled fines, into a granulator unit to obtain granules and
(c) drying the granules obtained from step (b) in a drying unit, wherein elemental sulphur is introduced before the drying step.

The invention further relates to sulphur-containing ammonium phosphate fertilizers, to the use of these sulphur-containing fertilizers to promote the growth of agricultural products and to the agricultural products thus-obtained.

(Figure 1)

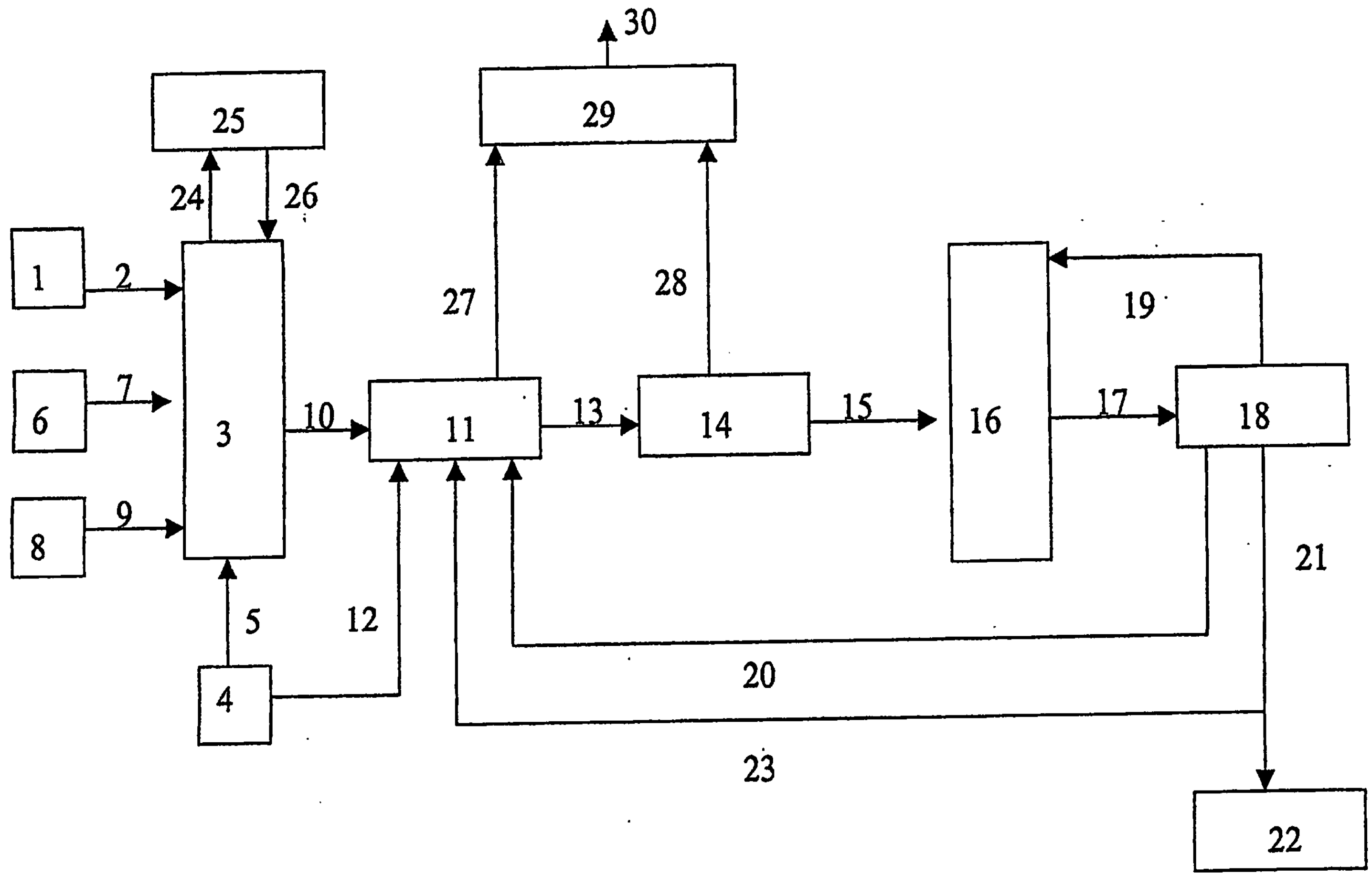

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Figure 1

PCT Application
PCT/EP2003/050821